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Impact of gas storage on reservoir rocks – long-term study to investigate the effects on mineral content and fluid chemistry

Monika Kasina[a,b], Daria Morozova[a], Marek Michalik[b], Dieter Pudlo[c], Hilke Wuerdemann[a]*

[a]*German Research Centre for Geosciences GFZ,Section 4.5 Geomicrobiology,14473 Potsdam, Germany*
[b]*Institute of Geological Science, Jagiellonian University, 30-063 Krakow, Poland*
[c]*Friedrich-Schiller-University Jena, Institute of Geosciences,Burgweg 11, D-07749 Jena, Germany*

Abstract

To study the effects of gas storage, long-term autoclave experiments with rock cores originating from a natural gas reservoir and brines taken from a gas well were conducted at 40 bar and 80° C in a CO_2 atmosphere. While the main mineral composition of the sandstones was not affected due to CO_2 exposure over a period of 31 months, the dissolution of rock-forming minerals such as feldspar, quartz or pore-filling anhydrite and calcite was noted. Changes in the brine composition were also detected. A release of iron and total organic carbon (TOC) from the rock samples to the saline fluid was observed. Temporary changes in the acetic acid concentration might have contributed to the dissolution processes. Precipitation and dissolution of minerals in sandstones were mostly related to diagenetic fluid-rock reactions and CO_2 exposure, but in general the impact of CO_2 on rock composition was only minor.

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Keywords: CO_2 storage; mineral-brine interaction; mineral dissolution and precipitation.

* Corresponding author. Tel.: +49331 288 1516; fax: +49331 2300 662.
*E-mail address:*wuerdemann@gfz-potsdam.de

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1. Introduction

The transition of the energy supply from nuclear and CO_2-emitting power plants to renewable energy is fundamental for sustainable energy generation in the future and important for mitigating climate changes due to greenhouse gas emissions [1]. A transition to renewable energy sources requires large-scale energy storage capacities due to fluctuation in energy supply. New storage technologies are necessary to make this transition successful. One possible method of storing excess energy is to transfer it to hydrogen or methane, which can subsequently be injected and stored in subsurface porous rock formations like depleted-gas reservoirs and presently used gas storage sites [2]. This allows the storage of large amounts of energy. However, processes such as the migration of reservoir fluids to the upper formations, possible leakages of injected gases, groundwater contamination and geochemical as well as biological changes are possible [3]. Therefore it is necessary to understand and predict processes that might affect storage efficiency and the environment.

In order to investigate the feasibility of hydrogen storage in the subsurface, the collaborative project H2STORE ("hydrogen to store") was initiated [2]. In the scope of this project, potential reactions between microorganisms, fluids and rocks induced by the stored gas are studied. In gas storage, CO_2 can be used as a pillow gas, therefore it is important to increase the knowledge concerning the effects of CO_2 on the reservoir rocks and the chemical composition of reservoir fluids. Potential geological reservoirs for gas storage contain complex geochemical systems, including a broad diversity of minerals and brines. Changes in the reservoir conditions arising from the storage process may influence the efficiency as well as the long-term safety of gas storage in the subsurface.

In order to study the changes in the mineral composition and the fluid chemistry under the influence of CO_2 exposure, long-term laboratory experiments were performed. The aim of the study is to monitor the effects of CO_2 exposure on minerals and reservoir brines using chemical analyses, scanning electron microscopy with energy dispersive spectrometer (SEM-EDS) and X-Ray diffraction analyses.

2. Materials and Methods

2.1 Study area and sampling

The studied depleted natural gas reservoir site is located in the North German Basin at a depth of about 3500 m. The brine is characterized by a salinity of up to 420 g L^{-1}. The reservoir pressure is 200 bar and the temperature varies between 120 and 130° C. It consists of Rotliegend sedimentary rocks composed of laminated claystones, siltstones and sandstones [4].

The sandstone samples from the reservoir were collected from the core repository. A detailed description of the sandstones is given by [5] and [6]. The experiment samples were milled to a size of 0.5 cm. Fresh brine samples were collected from the reservoir by downhole sampling (Erdöl-ErdgasWorkover GmbH) at depths between 3000 and 3500 m. A detailed description of the fluid sampling procedure is available in [7]. The fluids were transferred aseptically into sterilized glass vials, refrigerated to 4° C and immediately transferred to the laboratory. Chemical analyses of the reservoir brine were performed prior to the long-term experiments and are summarized in [7].

2.2 Set-up of the experiment

Milled rock samples and reservoir fluids were incubated in corrosion-resistant high-pressure vessels to apply elevated temperatures and pressure conditions. The pressure vessels were cleaned with a rinsing agent and pure water and dried overnight at 105° C in an oven. Prior to the experiment, pressure vessels were disinfected with a 1% NaOCl solution. Incubation was performed at 80° C and a pressure of 40 bar with 150 mL of reservoir fluid and 100 g of rock. After an equilibration period of three months with the saline fluids, the milled samples were exposed to CO_2 for 2.5 years. One sample was exposed to pure N_2 as a control. Two sampling series were performed, after 11 and 31 months of CO_2 exposure. From each vessel 10 mL of fluid and 5 g of rock pieces were sampled for chemical and mineralogical analyses respectively.

2.3. Analytical methods

2.3.1 Chemical analyses of the brine

Cations and anions in the saline fluids were detected using inductively coupled plasma – mass spectrometer (ICP-MS) and inductively coupled plasma optical – emission spectrometry (ICP-OES) methods. The organic acid concentration was measured using a gas chromatography mass spectrometry (GC/MS), and the TOC was analyzed using a carbon analyzer (DIMATEC GmBH, Essen, Germany) according to the DIN EN 1484-H3 norm.

2.3.2 Mineralogical analyses

Prior to the analyses, the samples were washed using distilled water in order to remove salt from the rock surface and subsequently dried in the oven at 50° C and crushed. In addition, for x-ray powder diffraction, samples were milled in an agate mill to the fraction <0.02 mm.

To identify the main mineral components before and after CO_2 exposure x-ray powder diffraction (XRD) was used. A diffractometer Bruker-axs D5000 with 2Theta goniometer was applied. The analytical range used for analyses was 15–65°θ, step width 0.02°, and the time 1s/step, using a CuKα radiation. For phase identification, the DIFFRACplus software was used. Samples were pressed into analytical cuvettes.

To characterize the structure and the spatial relationship between rock components as well as the mineral phases and their chemical composition a scanning electron microscope (SEM) Hitachi S-4700 was used. Quantitative analyses of the chemical composition of the minerals were performed using an energy dispersive spectrometer (EDS). To identify elements the analytical software NSS 2.2 was applied, which provided spot analysis of the chemical composition of the samples and a distribution of elements. Results were recalculated to 100% according to the standardless quantification procedure using the option of automatic or manual search of elements. The sandstone pieces were carbon coated and examined with a scanning electron microscope operating at an accelerating voltage of 20 kV, using the secondary electron (SE) signals.

3. Results

3.1 Changes in chemical composition of the brine

After 31 months of incubation at 40 bar and 80^{o} C, changes in the concentration of some major and minor elements in the brine were noted in all vessels exposed to CO_2. However, most of the changes were in the range of the accuracy of the methods, e.g. for the majority of heavy metals. As an example for such minor variation in major element content, Fig. 1 shows the variations of calcium concentrations measured after 11 and 31 months. A distinct increase in iron concentrations in the saline fluid was observed in most of the vessels (Fig. 1). While the iron increase was in average 30 % after 11 months of CO_2 exposure, the concentration was only about 20% higher referring to the baseline after 31 months, except for vessel 6. For vessel 6, we observed a decrease of 25% referring to the baseline. In the control vessel exposed to nitrogen (N_2) a decrease in iron concentration of 30% was detected in both samplings. The concentration of acetic acid increased temporarily in most of the vessels, except no. 5 and 7, and after 31 months it decreased to the level before CO_2 exposure. The total organic carbon (TOC) concentration increased by a factor of three after 11 months and remained on this level until the end of the experiment, except for vessel 1. However, in the control vessel the TOC concentration increased by a factor of 10 after 11 months of exposure and by a factor of 40 after 31 months (Fig. 1). The pH remained at 5.5 during the whole experiment in all vessels.

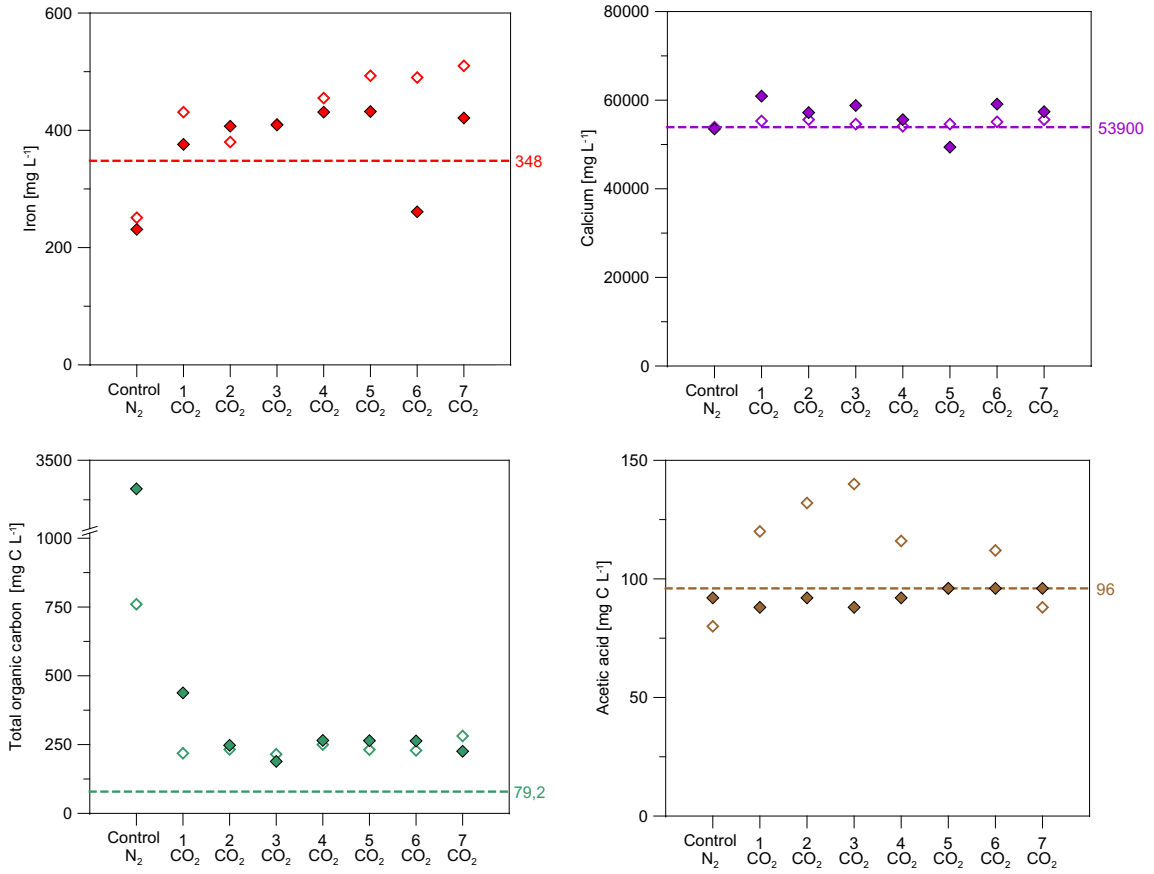

Fig. 1. Iron (red); calcium (violet); total organic carbon (TOC) (green) and acetic acid (brown) concentrations
---- - before experiment, after 11 months (cubes) and after 31 months (filled cubes)

3.2 Mineral composition of sandstones before and after CO_2 exposure.

The main minerals determined in sandstones using XRD are quartz, albite, K-feldspar, calcite, dolomite and anhydrite. The composition did not change during the 31 months of CO_2 exposure (Fig. 2). However, some changes were noted in the relative peak intensities, most probably indicating some dissolution and crystallization of minerals. SEM analysis showed examples of dissolution of K-feldspar (Fig. 3a) and pore-filling anhydrite as well as the precipitation of secondary albite (Fig. 3b), quartz and clay minerals in the pore spaces and on the authigenic minerals.

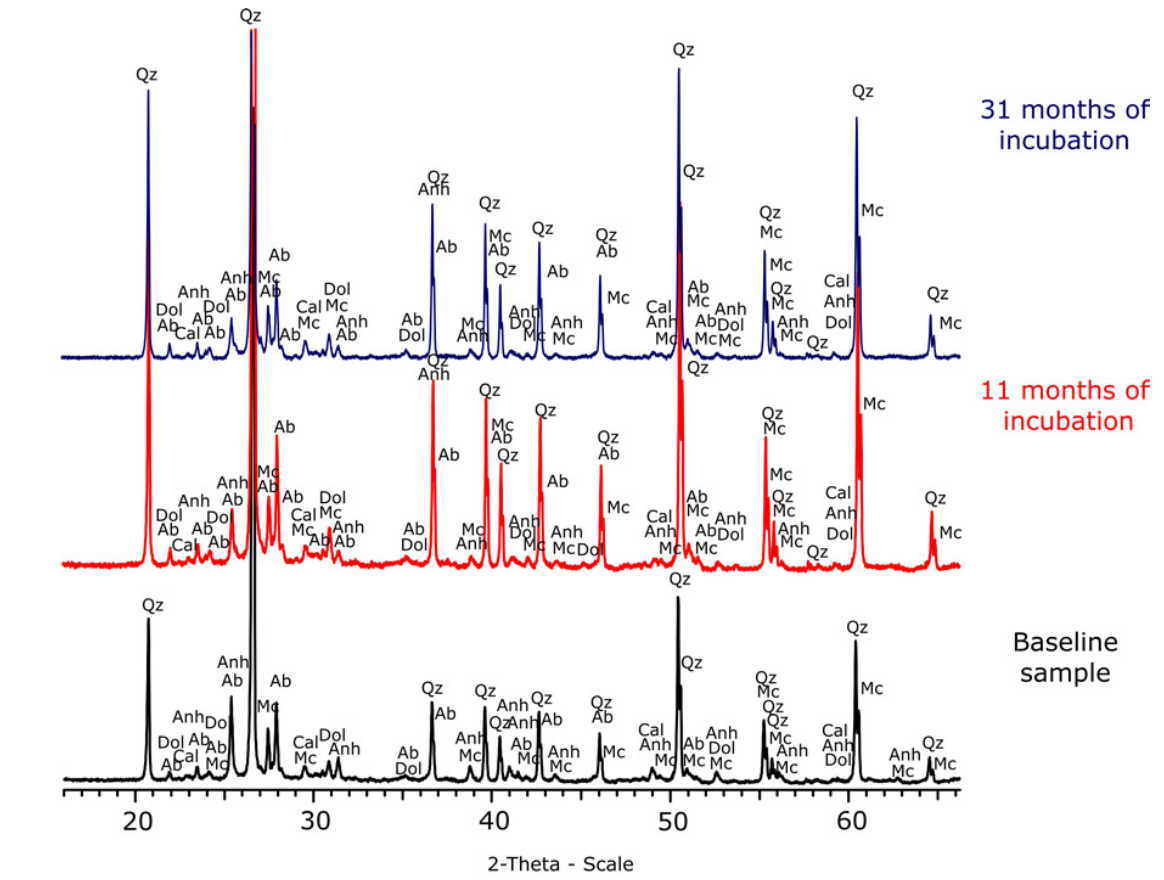

Fig. 2. X-Ray diffraction patterns. Qz – quartz, Ab – albite, Mc – microcline, Anh – anhydrite, Cal – calcite, Dol – dolomite. Vertical scale is relative. Lin(counts) in the range of dozens of thousands counts

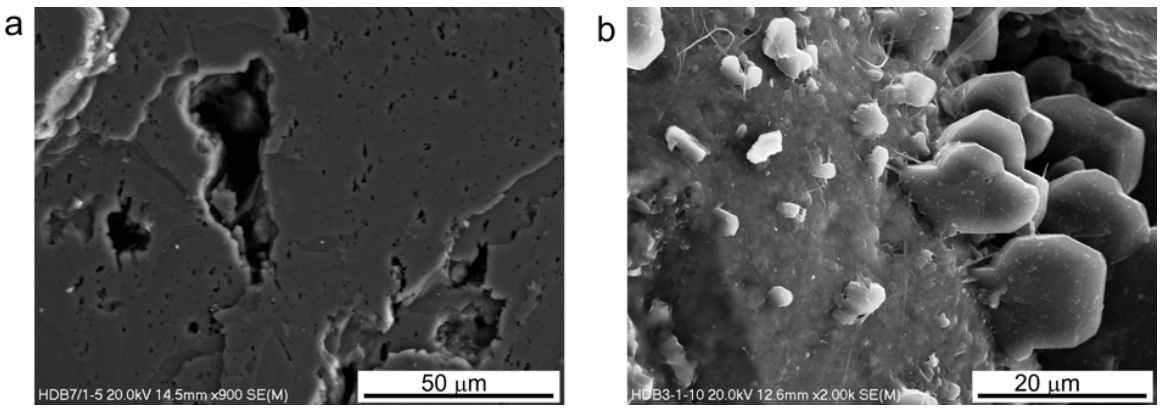

Fig. 3. SEM-SE pictures of dissolution pits in K-feldspar (a); newly precipitated albite (b);

4. Discussion

Long-term CO_2 exposure at a temperature of 80º C and a pressure of 40 bar did not affect the main mineral components of the sandstones over a period of 31 months. However, slight changes in XRD peak intensity indicate the initial dissolution of silicates like feldspar and quartz and cements such as anhydrite, calcite and dolomite as well as the precipitation of secondary phases such as albite or quartz. These results were consistent with the SEM-EDS analyses. Partial dissolution of silicates was also noted by [8] after injection of CO_2. Furthermore, temporary increase of acetic acid concentration, observed after 11 months of CO_2 exposure, might have contributed the dissolution of aluminosilicates or quartz as suggested by [9].

The distinct increase in iron concentration might have resulted from the dissolution of carbonates (iron-containing dolomite), or other iron rich minerals (chlorite, iron oxides). The dissolution of carbonate cements was also observed in other studies [9,10,11]. As suggested by [8], iron (hydro)oxides dissolve in a CO_2 atmosphere and at acidic pH. Similar observations were made by [12]. They related the increase in iron to the dissolution of iron (hydro)oxides. According to [13] low pH (5,5) in the presence of CO_2 can induce mineral dissolution and thus, metal mobilization including heavy metals and potentially toxic elements. However, in our study only slight changes for heavy metals and toxic elements in the range of the accuracy of the method were observed.

5. Conclusion and outlook

In general, 31-months incubation of rock samples and reservoir brines with CO_2 at 80^{o} C and 40 bar did not affect the system strongly. Precipitation of secondary phases and dissolution of rock forming minerals and cements were mainly related to fluid-rock reactions that were enhanced by CO_2 exposure. As a continuation of these experiments, samples are being exposed to a hydrogen atmosphere to study the effects on the reservoir rocks.

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